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(54) Title: PACKAGING MATERIAL AND METHOD FOR MANUFACTURING THE SAME

(57) Abstract: The present invention provides a cost-effective method for manufacturing packaging materials having oxygen and moisture barrier properties, comprising applying a coating of ethylene vinyl alcohol to the substrate film and wherein the coating of ethylene vinyl alcohol is applied using a solution with an ethylene content of between 4 and 18%mol.

## Packaging Material and Method for Manufacturing the Same

The present invention relates to improvements in packaging materials, and in particular in packaging materials with reduced oxygen and moisture permeability.

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When packaging food and other products that are sensitive to degradation due to oxidation, it is the normal practice to use packaging materials which act as a barrier to oxygen transmission. Products that are moisture sensitive also need protection and are packaged using materials which act as a barrier to moisture.

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Conventionally, barrier properties are afforded in these films by solution coating or extruding barrier resins such as PVDC, EVOH or PVOH onto or with the film, or by depositing materials such as aluminium, aluminium oxide and silicon oxide onto the surface of the film by various means.

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All of these conventional methods have the desired effect of producing the required barrier properties. However, materials produced using the conventional methods are expensive, for example, because they involve additional processes after the film has already been produced.

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It is the aim of the present invention to provide a cost-effective method of producing packaging films that exhibit oxygen and moisture barrier properties. The barrier coating is preferably applied during the production of the film itself.

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Oriented packaging films are commonly manufactured using a two-step process whereby an extruded film is stretched in a first direction, for example using a so-called MDI machine. After exiting the MDI machine, the film may or may not be chemically treated using an "in-line" coater, for example, to improve the adhesion properties of the film. Then, the film is stretched in a second direction,

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perpendicular to the first direction, i.e. in a transverse direction. This may be done in a so-called TDI machine.

Thus, it is known in the art to apply coatings "inline" on a film production line. The coating may be applied immediately after the film is extruded and before the films are stretched, or between the two stretching steps, that is, between the MDI machine and the TDI machine.

5

Because a film produced by the above-discussed method is generally stretched by a factor of between 4 and 60 times, the thickness of the coating in the final product will generally be very thin, normally between 0.05 and 0.3 microns in thickness.

Thus, most barrier coatings applied in this conventional way do not exhibit  
10 sufficient barrier properties. The use of PVDC, for example, does not improve the barrier properties of the film significantly enough for the coated films to be commercially viable.

The present invention relates to use of barrier resin ethylene vinyl alcohol (EVOH)  
15 in the production of films that exhibit high oxygen and moisture barrier properties. EVOH is known to have oxygen barrier properties and is frequently applied to films in order to render them oxygen impermeable.

However, the present invention seeks to apply the EVOH barrier coating in a more  
20 economical manner, whilst still producing a packaging film with the desired barrier properties. Furthermore, the invention overcomes many problems known to be associated with the application of EVOH coatings to packaging films.

In the past, EVOH coating has been difficult to handle and to apply because the  
25 standard 30-50% ethylene containing EVOH is difficult to hold in solution. Furthermore, it is also difficult to adhere EVOH coatings to normal films such as OPET (oriented polyester), OPP (oriented polypropylene) and OPA (oriented polyamide or nylon). Therefore, an EVOH coating has previously generally required a tie layer or primer that will adhere it to these films.

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A further problem is that an EVOH coating, when applied in this way, does not achieve the desired oxygen barrier property, which is defined as the transmission of

a maximum of 20ccs of oxygen through 1 square metre of film per day at 23°C and a relative humidity (RH) of 75% or more with 100% oxygen on one side of the film.

In light of the above-mentioned problems encountered when coating films, it is the  
5 current practice of some manufacturers to apply a coating of PVOH that is crosslinked with a suitable crosslinker and catalyst between the MDI and TDI machines. In such a process, roughly 0.1 micron of coating remains on the film after manufacture and oxygen transmission figures of between 3 to 10ccs are obtained.

10 However, even after crosslinking, PVOH is moisture sensitive and a laminate made out of a PVOH coated film will tend to delaminate when in moist conditions, for example, when a tray is filled with a very wet product and is lidded with a PVOH coated film laminate. Thus, packaging materials with PVOH coatings will not be suitable for many packaging applications and are only suitable for dry products.

15 The present invention provides an EVOH solution suitable for coating films. The handling problems encountered in connection with EVOH solutions are overcome by reducing the ethylene content of the EVOH to between 4 to 18%mol, and preferably to between 7 to 14%mol. This allows the EVOH to become easily  
20 dissolved in water. In a preferred embodiment, the EVOH is dissolved in a blend of an alcohol such as isopropanol and water. Alternatively, the alcohol may be propan-1-ol or propan-2-ol. In a further preferred embodiment, the EVOH solution does not include a dispersion stabilising agent. In particular, the solution does not require a stabilising agent of the nature disclosed in European patent application no.  
25 0 525 205 (Kuraray Co. Ltd.).

Preferably, the EVOH is between 90 and 99.99% hydrolysed. In a more preferred embodiment, the EVOH is between 99 and 99.99% hydrolysed, which produces a coated film with the best gas barrier properties.

30 In another preferred embodiment of the invention, a small percentage of between 10 to 25% of partially hydrolysed EVOH (85% to 90% hydrolysed) is incorporated into the solution. This helps to improve the adhesion of the EVOH to the base

film without affecting the gas barrier property and makes the solution easier to handle.

Preferably, the degree of polymerisation of the EVOH is not larger than 1500 and is more preferably between 150 and 400. This is because a degree of polymerisation greater than 1500 will render the viscosity of the solution too high to handle on a coating machine. The degree of polymerisation is measured according to JIS K6726.

In order to apply the coating of EVOH, a solution preferably comprises between 5 and 20% by weight EVOH, an even more preferable concentration being between 8 to 15% by weight.

In yet another preferred embodiment of the invention, a crosslinking agent is added to this solution before applying the coating to the film. The preferred crosslinking agent is glyoxal, but other crosslinking agents such as methylated melamine formaldehyde, trimethylol melamine urea formaldehyde, borax, urea, colloidal silica etc. may be used. Preferably, the amount of glyoxal added is between 5 and 25%mol.

The general practice with such solutions is to add approximately 1% of an acid catalyst, such as orthophosphoric acid, ammonium nitrate, ammonium sulphate, sulphuric acid, ammonium chloride, sodium acetate, nitric acid, etc. However, this practice means that the adhesion of the EVOH coating to the film substrate is not good enough for use. In order to overcome this adhesion problem, one would usually use a primer or add an adhesive substance to the EVOH, which would achieve sufficient adhesion. However, the use of adhesive in an EVOH coating is not satisfactory as it leads to loss of barrier property and the bond obtained is not reliable.

Therefore, in a further preferred embodiment of the invention, the EVOH is keyed to the base film without the use of primer or the addition of adhesive in the EVOH solution. This is achieved by the addition of very low quantity of sodium acetate, or other such salts of different elements, to the mixture of EVOH and crosslinking

agent. Very low quantities of the other acids enumerated above may be used, however sodium acetate is the preferred agent. The quantity added is preferably between 0.01% to 0.2%mol. More preferably, the quantity of sodium acetate added is between 0.01% to 0.1%mol. The use of such a small quantity in the mix achieves  
5 100% adhesion of the EVOH to the base film once the resultant film is heated to a minimum temperature of 90°C for a short time of between 3 to 60 seconds. The preferred temperature is 100°C or more.

The coating of the invention may be applied to different films. When used for  
10 polyester film, the film surface should preferably be treated with such conventional treatment as corona discharge or flame treatment before the coating is applied. However, such pre-treatment of the polyester film surface is not essential, as adhesion can be achieved without it.

15 When coating an OPP film, it is necessary to modify the polymer on the side to be coated. Generally OPP films are co-extruded with 3 layers with the core layer and two outer layers. The layer that is to be coated has to be changed to either 100% maleated polypropylene (maleic anhydride modified polypropylene) or a percentage of maleated polypropylene has to be added to the existing polypropylene being  
20 used. The addition rate has to be to the order of around 10% to 20%. The maleic polypropylene is sold under various names such as Admer, Plexar and Bynel (all registered trademarks).

Oriented nylon films may also be coated using the invention, provided that the side  
25 of the film to be coated is suitably modified by corona, flame or other treatments that are well known to those experienced in the art.

A further advantage of the invention is that the adhesion of the EVOH coating is strong enough to allow such coatings to be applied to shrinkable films. The EVOH  
30 coating may be used when producing barrier shrinkable films from OPET, OPP and OPA. Such films are used for primal cuts of meat, for flow wrapping and for lidding applications.

A further feature of this invention is that whilst this technology provides an excellent barrier to gases such as oxygen, the moisture barrier property is not enhanced and remains the same as the base film.

- 5 In yet a further embodiment of the invention, the film may be metallised on either side with a metal, preferably aluminium. Alternatively, the film may be coated with aluminium oxide, silica oxide or a clay type coating. Such treatment produces film with extremely high oxygen barrier properties, the film having a transmission rate of less than 1cc. In addition, moisture barrier property of the film is also increased to  
10 a very high level, achieving a moisture transmission at 38°C, 90% relative humidity of 1g or less per m<sup>2</sup> per day.

The metallisation or coating can be done on either side of the EVOH coated film but it is preferably added to the side already coated with the EVOH, in order to  
15 further protect that side.

In one embodiment of the invention, the EVOH coating is applied during the production of the film itself as an "inline" coating process.

- 20 In an alternative embodiment of the invention, the EVOH coating is not applied during the further conversion process of the film. The coating can be employed "offline", allowing a greater weight of coating to be applied.

The coating can be applied directly to corona treated OPET, or to suitably modified  
25 OPP or OPA, with or without a primer. In the case of OPET, a coating weight of 2 grams per square metre achieves an oxygen transmission of 0.02ccs (at 23°C, 75% RH, per m<sup>2</sup> per day. This is the measurement method used in all further references to the oxygen transmission rate, unless otherwise stated). In the case of OPP, a transmission rate of around 3ccs is achieved.

30

A virtually impermeable film is obtained when the offline-coated films are metallised or suitably coated.

When these films are metallised or suitably coated as described above, transmission rates become very significant. In the case of OPET, the rate of transmission is not measurable by standard Mocon equipment and the film can be considered to be impervious to oxygen to the same extent as aluminium foil. The advantage of a film according to the invention over aluminium foil is that this film is not liable to pin holes, as aluminium foil is and the ability to recycle the product is much improved. In the case of OPP, the oxygen transmission rate is less than 0.5ccs.

#### 10 Example 1

A 12-micron thick, corona treated, polyester (PET) film was coated on the treated side with crosslinked EVOH as described according to the invention. A coated weight of 1.5gms of EVOH was obtained in the finished film. Part of this film was held and part was then metallised on the EVOH side. Some of these films were laminated with solventless polyurethane adhesive to a 50 micron thick PE film. The results obtained with these films are listed in Table 1.

#### 20 Example 2

A 12-micron thick PET film was produced on a stenter film line and a coating of crosslinked EVOH was applied between the machine direction orienter and the transverse direction orienter. Part of this film was held and part was then metallised on the EVOH side. Some of these films were laminated with solventless polyurethane adhesive to a 50 micron thick PE film. The results obtained with these films are listed in Table 2.



Table 1

Film	O <sub>2</sub> trans at 23°C, 85% RH per day	MVTR 38°C, 85% RH/m <sup>2</sup> per day	Adhesion of coating bond to base film	Laminate integrity when minced beef flowpacked in film at ambient temp	Laminate integrity when minced beef flowpacked in film at chiller temperature 4°C	Laminate integrity when minced beef flowpacked in film at freezer temp at -30°C
EVOH coated PET	0.03 ccs	10.3 gms	Over 500 gms/15m m	No signs of delamination	No signs of delamination	No signs of delamination
EVOH coated PET metallised	Not measurable	0.7 gms	Over 500 gms /15mm	No signs of delamination	No signs of delamination	No signs of delamination
EVOH- PET / PE50	0.03 ccs	3.2 gms	Over 500 gms /15mm	No signs of delamination	No signs of delamination	No signs of delamination
EVOH PET / PE50 metallised	Not measurable	0.3 gms	Over 500 gms /15mm	No signs of delamination	No signs of delamination	No signs of delamination

Table 2

Film	O <sub>2</sub> trans 23°C, 85% RH per day	MVTR 38°C, 85% RH /m <sup>2</sup> per day	Adhesion of coating bond to base film	Laminate integrity when minced beef flowpacked in film at ambient temp	Laminate integrity when minced beef flowpacked in film at chiller temperature 4°C	Laminate integrity when minced beef flowpacked in film at freezer temp at -30°C
EVOH coated PET	5.2 ccs	10.3 gms	Over 500 gms /15mm	No signs of delamination	No signs of delamination	No signs of delamination
EVOH coated PET metallised	0.26 ccs	0.73 gms	Over 500 gms /15mm	No signs of delamination	No signs of delamination	No signs of delamination
EVOH- PET / PE50	4.9 ccs	3.2 gms	Over 500 gms /15mm	No signs of delamination	No signs of delamination	No signs of delamination
EVOH PET / PE50 metallised	0.28 ccs	0.35 gms	Over 500 gms /15mm	No signs of delamination	No signs of delamination	No signs of delamination

## Claims

1. A method for manufacturing a packaging material, comprising applying a coating of ethylene vinyl alcohol to a substrate film and wherein the coating  
5 of ethylene vinyl alcohol is applied using a solution with an ethylene content of between 4 and 18%mol.
2. A method as claimed in claim 1, wherein the ethylene content is between 7 and 14%mol.
- 10 3. A method as claimed in either of the preceding claims, wherein the ethylene vinyl alcohol is dissolved in water.
4. A method as claimed in either of claims 1 and 2, wherein the ethylene vinyl  
15 alcohol is dissolved in a blend of an alcohol and water.
5. A method as claimed in claim 4, wherein the alcohol is isopropanol, propan-1-ol or propan-2-ol.
- 20 6. A method as claimed in any of the preceding claims, wherein the ethylene vinyl alcohol is between 90 and 99% hydrolysed.
7. A method as claimed in claim 6, wherein the ethylene vinyl alcohol is between 99 and 99.9% hydrolysed.
- 25 8. A method as claimed in any of the preceding claims, wherein between 10 and 25% of partially hydrolysed ethylene vinyl alcohol is incorporated into the ethylene vinyl alcohol solution.
- 30 9. A method as claimed in any of the preceding claims, wherein the polymerisation of the ethylene vinyl alcohol is no greater than 1500.

10. A method as claimed in claim 9, wherein the polymerisation of the ethylene vinyl alcohol is between 150 and 400.
11. A method as claimed in any of the preceding claims, wherein the coating  
5 solution is 5-25% ethylene vinyl alcohol by weight.
12. A method as claimed in claim 11, wherein coating solution is 8-15% ethylene vinyl alcohol by weight.
- 10 13. A method as claimed in any of the preceding claims, wherein the coating solution also comprises a crosslinking agent.
14. A method as claimed in claim 13, wherein the crosslinking agent is glyoxal, methylated melamine formaldehyde, trimethylol melamine urea  
15 formaldehyde, borax, urea or colloidal silica.
15. A method as claimed in claim 14, wherein the crosslinking agent is glyoxal.
16. A method as claimed in any of claims 13-15, wherein the solution further  
20 comprises 0.01% to 0.2%mol sodium acetate, or other such salts of different elements.
17. A method as claimed in claim 16, wherein the solution comprises 0.01% to 0.1%mol of an acid catalyst  
25
18. A method as claimed in claim 17, wherein the acid catalyst is orthophosphoric acid, ammonium nitrate, ammonium sulphate, sulphuric acid, ammonium chloride, sodium acetate or nitric acid.
- 30 19. A method as claimed in claim 18, wherein the acid catalyst is sodium acetate, or other such salts of different elements.

20. A method as claimed in any of the preceding claims, wherein the substrate film is polyester, polypropylene or polyamide, oriented films of these materials, or heat-shrinkable oriented films of these materials.
- 5 21. A method as claimed in any of the preceding claims, wherein the substrate film is pre-treated prior to the application of the ethylene vinyl alcohol coating.
22. A method as claimed in any of the preceding claims, wherein the coated film  
10 is further coated with a metal.
23. A method as claimed in claim 22, wherein the metal is aluminium.
24. A method as claimed in any of claims 1-21, wherein the coated film is further  
15 coated with silica oxide, aluminium oxide or clay coating.
25. A method as claimed in any of the preceding claims, wherein the substrate film is extruded, stretched in a first direction, and then stretched in a second directions substantially perpendicular to the first direction  
20
26. A method as claimed in claim 25, wherein the ethylene vinyl alcohol coating is applied before the first stretching step.
27. A method as claimed in claim 25, wherein the ethylene vinyl alcohol coating  
25 is applied after the first stretching step and before the second stretching step.
28. A method as claimed in claim 25, wherein the ethylene vinyl alcohol coating is applied after the first and second stretching steps.  
30
29. A method for manufacturing a packaging material with barrier properties, substantially as described in any of the foregoing examples.

30. A packaging material comprising a substrate film and an ethylene vinyl alcohol coating.
31. A packaging material as claimed in claim 30, wherein the substrate film is polyester, polypropylene or polyamide, oriented films of these materials, or heat-shrinkable oriented films of these materials.
32. A packaging material as claimed in either of claims 30 and 31, further comprising a metal coating.
33. A packaging material as claimed in claim 32, wherein the metal is aluminium.
34. A packaging material as claimed in either of claims 30 and 31, further comprising a coating of silica oxide, aluminium oxide or clay coating.
35. A packaging material as claimed in any of claims 30-34 having oxygen and moisture barrier properties.
36. A packaging material, substantially as described in any of the foregoing examples.

## INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08J7/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☐ Further documents are listed in the continuation of box C☒ Patent family members are listed in annex

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# INTERNATIONAL SEARCH REPORT

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